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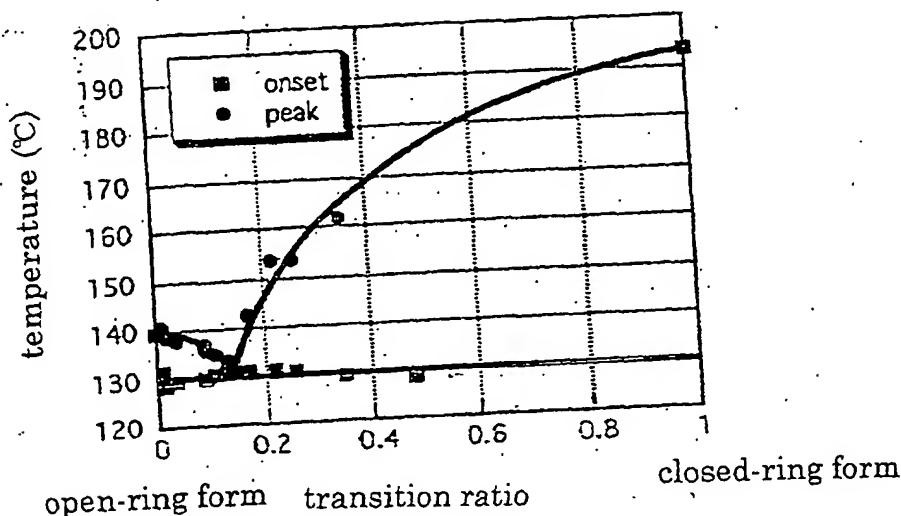
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(54) **ORGANIC MATERIAL UNDERGOING LIGHT-INDUCED PHASE TRANSITION**

(57) A photo-induced phase transition organic material is composed of a diheteroarylethene-based compound within which the photochromic reaction occurs in the crystalline state. The diheteroarylethene-based compound of the present invention reversibly changes in color with light irradiation and also changes in phase from the open-ring form in the crystalline state to the closed-ring form in the crystalline state, or from the

closed-ring form in the crystalline state to the open-ring form in the crystalline state via the liquid state, and can be applicable to optical recording media, display panels, sensors, optical switch devices and the like, by taking advantages of its variations in color with light irradiation and also its changes in physical property, such as the refractive index and the permeability, with its changes in phase.

Fig. 1a



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**Description****Field of the Invention**

5 [0001] The present invention relates to a photo-induced phase transition organic material, more particularly to a photo-induced phase transition organic material composed of a diheteroarylethene-based compound in which the phase transition occurs in response to light irradiation in a crystalline state, especially even in a single-crystalline state.

**Background of the Invention**

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[0002] A photochromic material, which means the material containing a sort of molecule or molecular assembly from which two isomers having different colors are reversibly formed due to the action of light, has been expected as a photo-functional material since a variety of its physical properties, such as not only the color, but also the dielectric constant, the oxidation/reduction potential, etc., reversibly varies with light irradiation in connection with its photochromic reaction. Both photochromic molecules and molecular assemblies conventionally employed are to be transferred with light irradiation from colorless state to one-colored state in a solution or a macromolecular medium, such as red and blue, while method of applying various chemical modifications to the photochromic molecules have been studied in order to obtain the photochromic material which can develop various colors.

**Object and Summary of the Invention**

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[0003] The present invention has arisen from the detailed analysis of the mechanism of the photochromic reaction of diheteroarylethene-based compound which does not need any dispersion medium, and the object of the present invention is to provide a photo-induced phase transition organic material which utilizes the photochromic reaction of diheteroarylethene-based compound.

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[0004] The photo-induced phase transition organic material of the present invention is composed of a diheteroarylethene-based compound within which the photochromic reaction occurs in the crystalline state, especially in the single-crystalline state.

[0005] On the other hand, conventional photochromic compound undergo the photochromic reaction in a state where they are dispersed or dissolved in a macromolecular film or a solvent, and there has been no photochromic compound which stably undergoes the photochromic reaction in a crystalline phase like the photochromic material of the present invention.

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**Brief Description of the Drawings**

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[0006] Fig. 1a and 1b are phase diagrams illustrating the relationship between the open-ring form/ring-closure form rate of a compound (II) to be obtained in the following Example of Synthesis 1 and its melting point, where Fig. 1a is a phase diagram in case of light irradiation and Fig. 1b is a phase diagram in case of a mixture.

**Detailed Description of the Preferred Embodiments**

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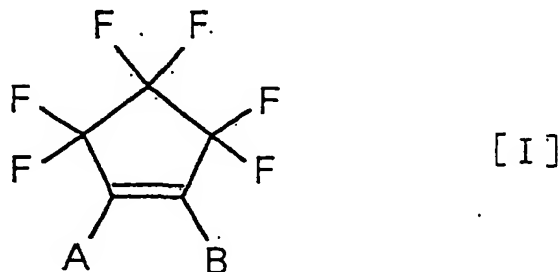
[0007] Hereinafter, embodiments of the present invention will be described in detail.

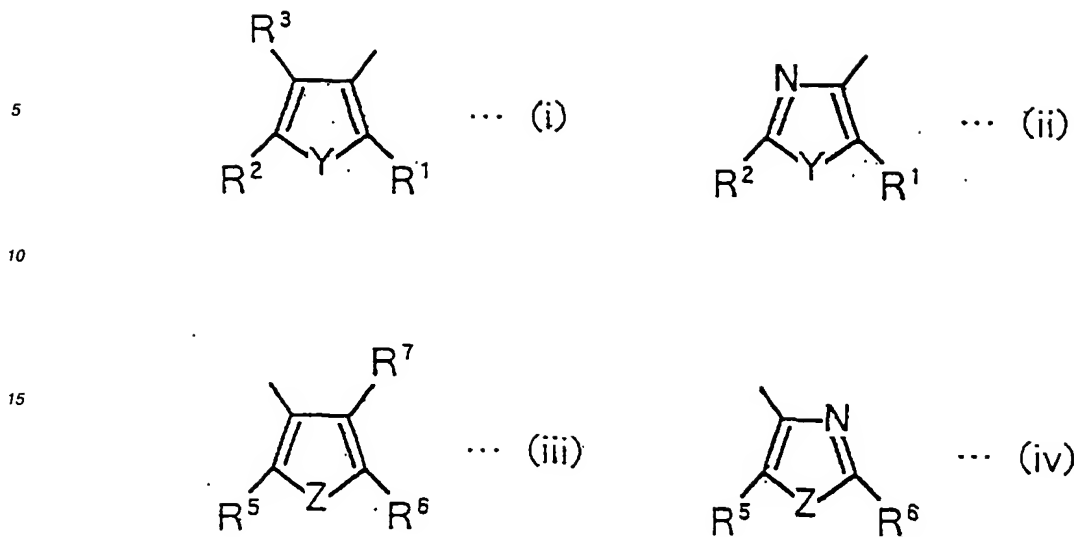
[0008] An example of the diheteroarylethene-based compound of the present invention is the one expressed by the following general formula [1]:

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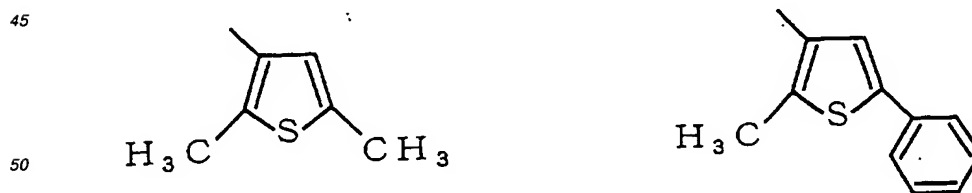


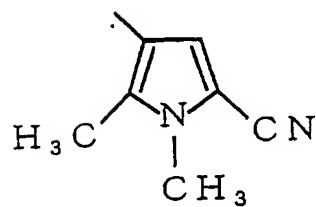
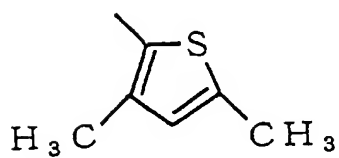
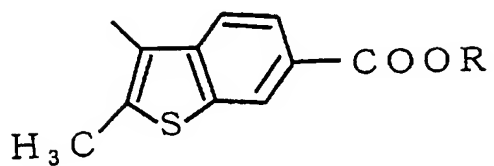
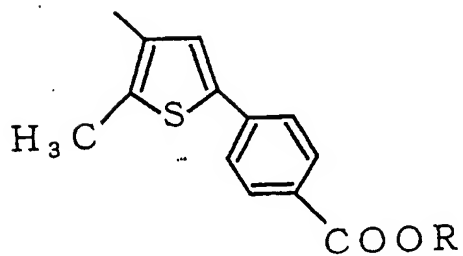
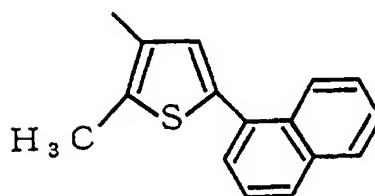
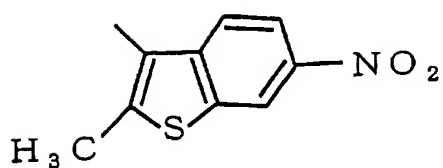
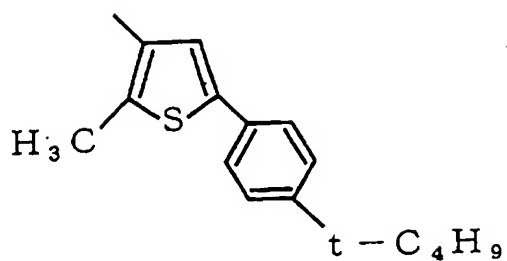
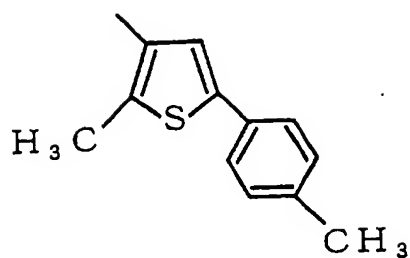


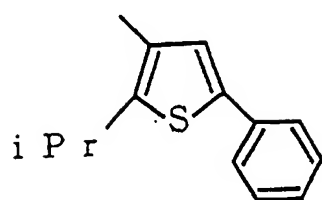
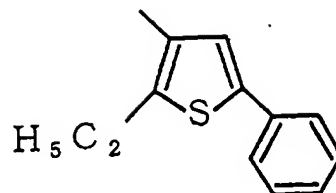
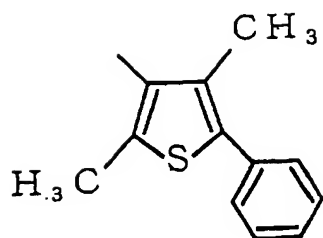
[0009] In the general formula [I], "A" expresses a substituent (i) or (ii). In the substituents (i) and (ii), "R<sup>1</sup>" expresses an alkyl group, an alkoxy group, a halogen atom, a trifluoromethyl group, a cyano group, or an aryl group which may have at least one substituent. "R<sup>2</sup>" and "R<sup>3</sup>" express a hydrogen atom, an alkyl group, an alkoxy group, a halogen atom, a trifluoromethyl group, a cyano group, an aryl group which may have at least one substituent, respectively, wherein "R<sup>2</sup>" and "R<sup>3</sup>" are independent of each other. Alternatively, "R<sup>2</sup>" and "R<sup>3</sup>" may be bonded to each other to form a carbocyclic ring which may have at least one substituent, or a heterocyclic ring which may have at least one substituent. "Y" expresses —O—, —S—, or —NR<sup>4</sup>— in which "R<sup>4</sup>" expresses a hydrogen atom, an alkyl group which may have at least one substituent, an aryl group which may have at least one substituent, or a cycloalkyl group which may have at least one substituent. "B" expresses a substituent (iii) or (iv). In the substituents (iii) and (iv), "R<sup>5</sup>" expresses an alkyl group, an alkoxy group, a halogen atom, or a trifluoromethyl group. "R<sup>6</sup>" and "R<sup>7</sup>" express a hydrogen atom, an alkyl group, an alkoxy group, a halogen atom, a trifluoromethyl group, a cyano group, or an aryl group which may have at least one substituent, respectively, wherein "R<sup>6</sup>" and "R<sup>7</sup>" are independent of each other. Alternatively, "R<sup>6</sup>" and "R<sup>7</sup>" may be bonded to each other to form a carbocyclic ring which may have at least one substituent, or a heterocyclic ring which may have at least one substituent. "Z" expresses —O—, —S—, or —NR<sup>4</sup>— in which "R<sup>4</sup>" expresses a hydrogen atom, an alkyl group which may have at least one substituent, an aryl group which may have at least one substituent, or a cycloalkyl group which may have at least one substituent.

[0010] Each of the above compounds transfers in phase from an open-ring form to a closed-ring form with ultraviolet irradiation, while being in the crystalline state.

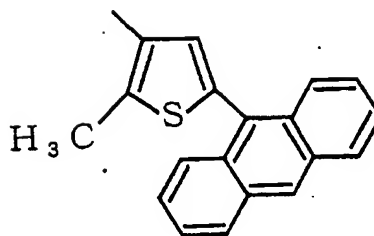
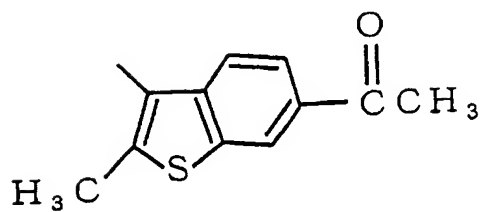
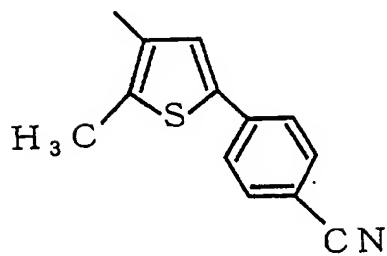
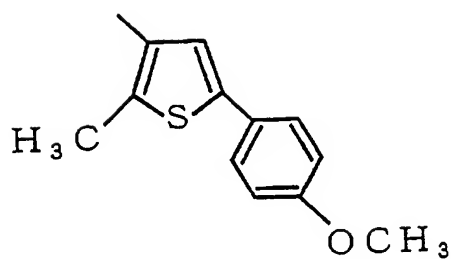
[0011] In the above general formula [I], the following substituents may be employed as substituents A and B, wherein "R" expresses an alkyl group or a phenyl group.





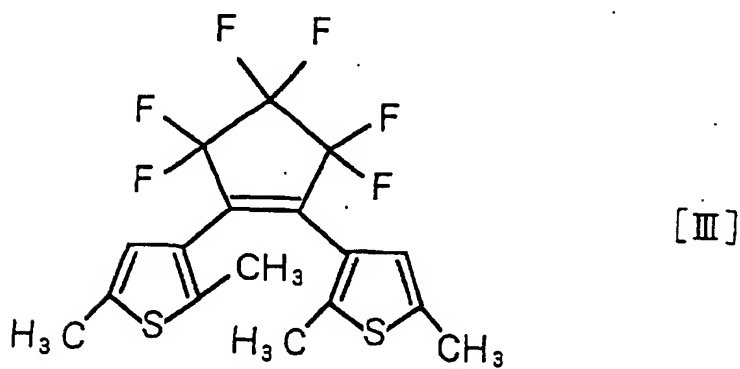
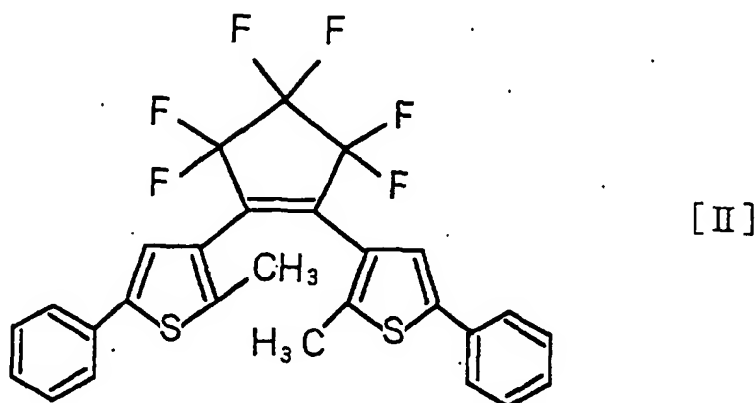


(iPr=isopropyl)



[0012] The diheteroarylethene-based compound is 1,2-bis(5-phenyl-2-methylthiophene-3-yl)perfluorocyclopentene

as expressed by the following formula [II]; or 1,2-bis(2,5-dimethylthiophene-3-yl)perfluorocyclopentene as expressed by the following formula [III]:



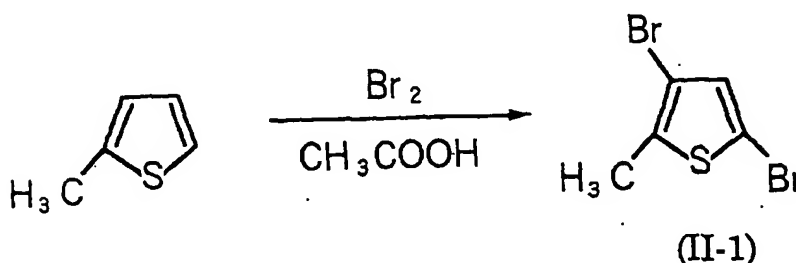
[0013] The diheteroarylethene-based compound is transferred in phase from the open-ring form to the closed-ring form with irradiation of ultraviolet having a wave length of about 300-400nm, and transferred in phase from the closed-ring form to the open-ring form with visible-light irradiation. The open-ring form differs from the closed-ring form in the melting point thereof.

[0014] Hereinafter, the present invention will be described in detail referring to examples of synthesis and examples of practice.

## Synthesis Experiment 1

[0015]

## [Synthesis of 3,5-dibromo-2-methylthiophene (II-1)]



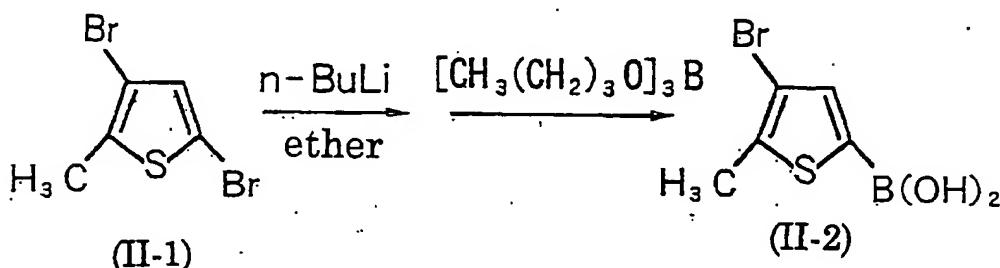
[0016] 2-methylthiophene of 25.4g (0.258mol) and acetic acid of 300ml were poured into a four-necked flask having a capacity of 1000ml, and then kept at a temperature of  $0^\circ\text{C}$  with an ice bath. Secondly, bromine of 82.5g (0.516mol) was slowly dropped into them with a dropping funnel, and acetic acid of 20ml was further added into them after the dropping, then the dropping funnel was washed. These ingredients were stirred for 30 minutes, while being kept at a temperature of  $0^\circ\text{C}$ . After that, the ice bath was removed and the ingredients were further stirred all night, while being warmed to a room temperature. The solution thus prepared was neutralized with sodium carbonate, added with a solution of sodium thiosulfate to perform ether extraction, washed with brine, and then dried with magnesium sulfate. The magnesium sulfate was removed by filtration after the drying and the ether was distilled off. The remainder was developed with hexane to separate a component of  $R_f=0.83$  by making use of a silica gel chromatographic column. The resultant was distilled under a reduced pressure in order further to separate a component having a boiling point 88 to  $90^\circ\text{C}$ . The yield of the compound (II-1) thus obtained was 34.7g, the rate of the yielding was 52.5%, and the results of NMR analysis were as follows:

$^1\text{H-NMR}$  (200 MHz,  $\text{CDCl}_3$ , TMS)

$\delta=2.34$  (s, 3H, Me)

6.86 (s, 1H, aromatic proton)

## [Synthesis of 3-bromo 2-methyl-5-thiophene borate (II-2)]



[0017] The above compound (II-1) of 34.7g (0.136mol) and anhydrous ether of 500ml were poured in a three-necked flask having a capacity of 2000ml, and then cooled to  $-60^\circ\text{C}$  or less. Secondly, 1.6N n-butyllithium of 87.6ml was incorporated into these ingredients and stirred for 30 minutes. After addition of 54.6ml tri-n-butyl borate, the ingredients were kept at a temperature of  $-60^\circ\text{C}$  or less for 4 hours, then warmed to a room temperature, stirred for 15 more hours, and further added with water to stop reaction. 1.2N hydrochloric acid was, then, added into the solution thus resulted in order to perform ether extraction. The ether phase thus appeared was further extracted with 1.0N sodium hydroxide solution. After that, the ether was removed, and then concentrated hydrochloric acid was added into the liquid phase until pH of the liquid phase corresponded to 1, while the liquid phase was kept  $0^\circ\text{C}$ , in order to separate the crystal. The crystal was filtered out by vacuum filtration and dried under reduced pressure, so that a compound (II-2) was

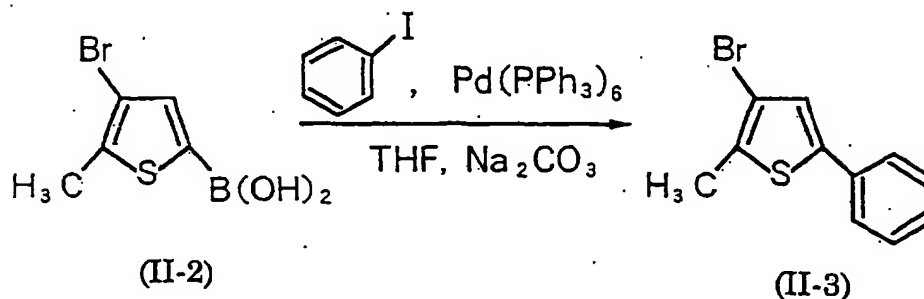
obtained. The yield of the compound (II-2) was 21.6g, the rate of the yielding was 72.2%, and the results of NMR analysis were as follows:

$^1\text{H-NMR}$  (200MHz,  $\text{CDCl}_3$ , TMS)

$\delta=2.46$  (s, 3H, Me)

7.35 (s, 1H, aromatic proton)

### [Synthesis of 3-bromo-2-methyl-5-phenylthiophene (II-3)]



[0018] The above compound (II-2) of 10.0g (45.3mmol), tetrahydrofuran of 70ml, sodium carbonate solution (20% by weight) of 70ml, iodobenzene of 7.6ml (68.0mmol) and tetrakis(triphenylphosphine)palladium (0) of 2.36g were poured in a three-necked flask having a capacity of 500ml, and then heated under reflux at 70°C for 2.5 hours in an atmosphere of argon. The solution thus prepared, then, was cooled down to a room temperature, applied with ether extraction, washed with a solution saturated with sodium hydrogen carbonate and water, and further dried with magnesium sulfate. The magnesium sulfate was removed by filtration after the drying and the ether was distilled off. The remainder was developed and separated by hexane by making use of a silica gel chromatographic column, and then recrystallized, so that a compound (II-3) was obtained. The yield of the compound (II-3) was 6.6g, the rate of the yielding was 57.6%, and the results of NMR analysis were as follows:

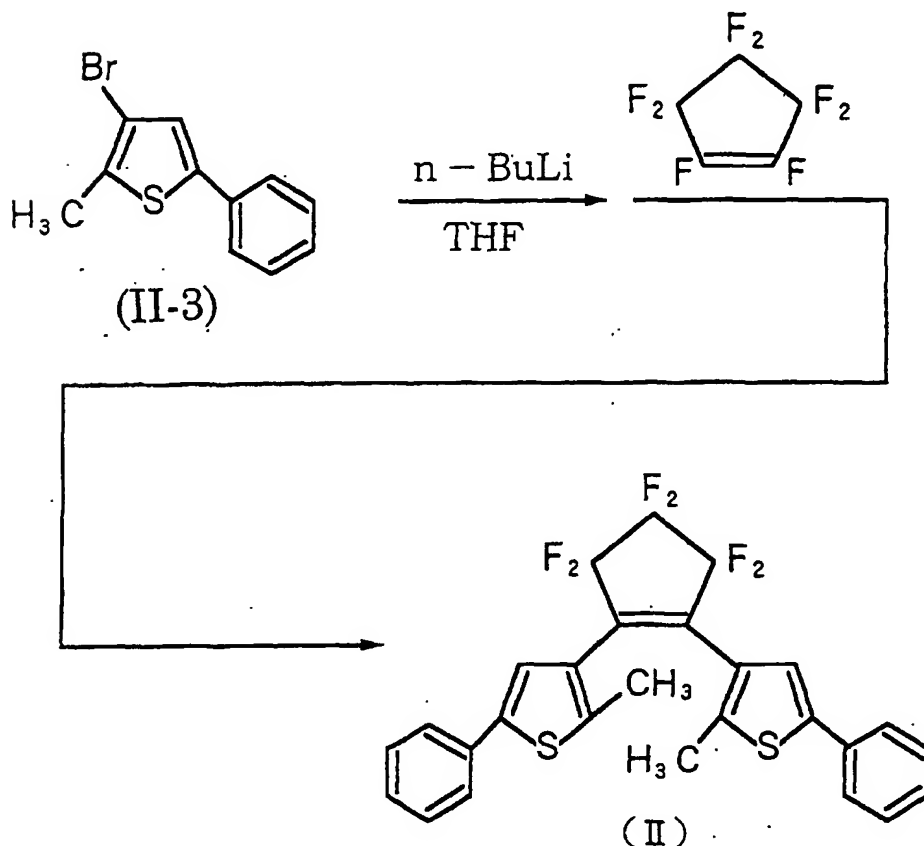
$^1\text{H-NMR}$  (200MHz,  $\text{CDCl}_3$ , TMS)

$\delta=2.41$  (s, 3H, Me)

7.10 (s, 1H, aromatic proton)

7.24-7.71(m, 5H, aromatic proton)





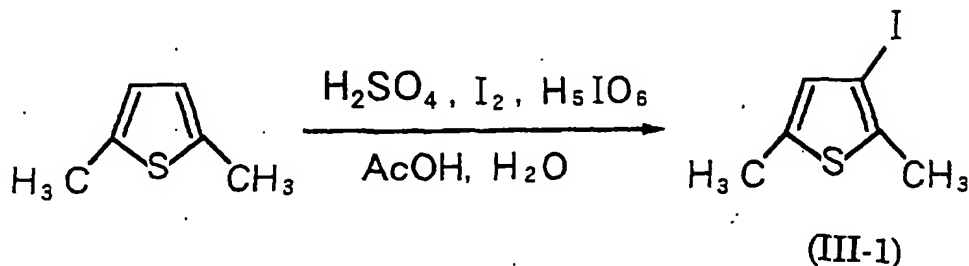
IR (KBr) : 3080, 3020, 2910, 1450, 1340, 1270, 1390, 1340, 1310, 1050, 990, 890, 760, 690cm<sup>-1</sup>

anal. Calcd for  $C_{27}H_{18}F_6S_2$ : C62. 30; H3. 4 9  
Found: C62. 66; H3. 72

## Synthesis Experiment 2

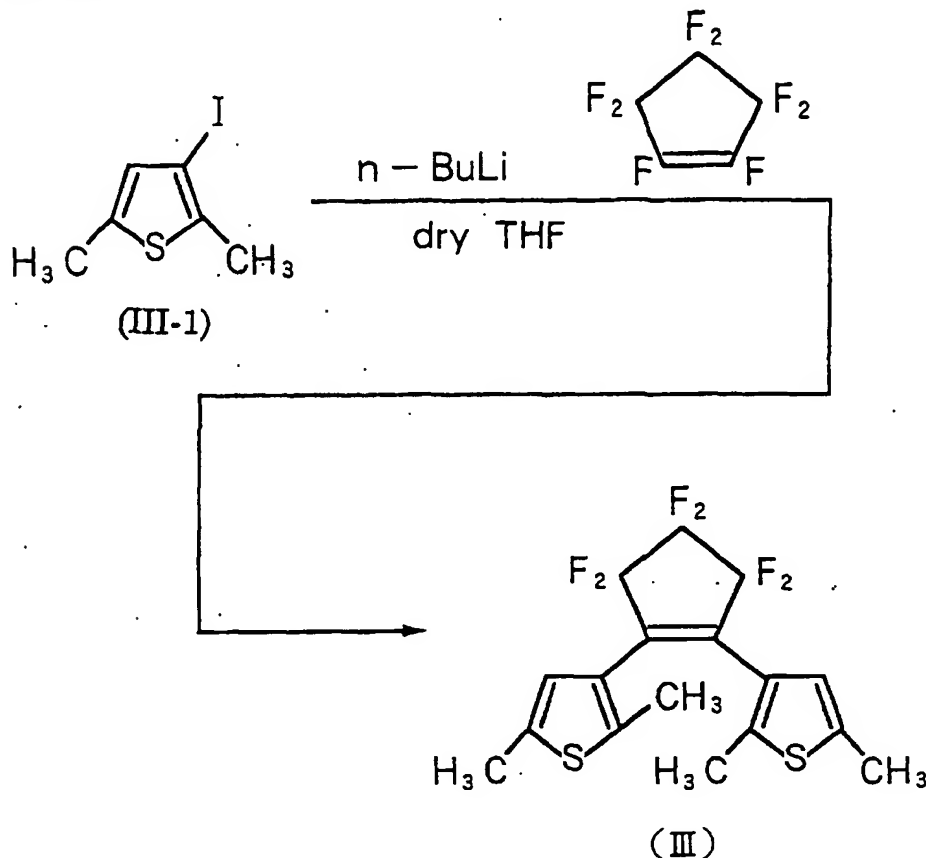
[0020]

### [Synthesis of 2,5-dimethyl-3-iodothiophene (III-1)]



[0021] Water of 75ml, concentrated sulfuric acid of 18ml, iodine of 11.4g and iodic acid of 3.5g were mixed into a solution of 11.2g 2,5-dimethylthiophene in acetic acid of 100ml, while the solution was stirred at a room temperature. The mixture was under reflux at 70°C for 2 hours, and then the reaction mixture was cooled by ice water. The mixture, further, was applied with ether extraction, and its organic layer was washed with water, a solution of sodium carbonate and a solution of sodium thiosulfate, then dried with magnesium sulfate. After that, the solvent was distilled off, and the remainder was developed by hexane by making use of a silica gel chromatographic column to isolate 2,5-dimethyl-3-iodothiophene (III-1). The yield of the compound (III-1) was 16.6g, the rate of the yielding was 70%, and the results of NMR analysis were as follows:

[Synthesis of 1,2-bis(2,5-dimethylthiophene-3-yl)perfluoro-cyclopentene (III)]



[0022] A solution of 1.6N n-butyllithium hexane of 36ml was dropped into a solution of 12.9g 2,5-dimethyl-3-iodothiophene (III-1) in xerotetrahydrofuran of 70ml, while the solution was cooled at  $-70^{\circ}\text{C}$  by dry ice-methanol bath in an atmosphere of argon, the solution was stirred for one hour, and then 2.5ml perfluorocyclopentene was dropped into the solution in three steps at intervals of 30 minutes. After being cooled with water, the mixed solution was warmed to a room temperature, and then the solvent was distilled off. The mixture, further, was extracted by ether, washed with brine, and then dried with magnesium sulfate. After that, the solvent was distilled off, and the remainder was developed by hexane by making use of a silica gel chromatographic column and recrystallized to isolate 1,2-bis(2,5-dimethylthiophene-3-yl)perfluorocyclopentene (III). The yield of the compound (III) was 6.94g, the rate of the yielding was 65%, and the results of NMR analysis were as follows:

$^1\text{H}$  NMR (200MHz,  $\text{CDCl}_3$ , TMS)

$\delta=1.81$  (6H, s, Me)

2.41 (6H, s, Me)

6.72 (2H, s, aromatic H)

Example 1

[0023] The single crystal (II-A) of the compound (II) was obtained from a solution of the compound (II) in hexane by the solvent evaporation method. The single crystal (II-A) was transparent and colorless. On the other hand, the closed-ring forms of the compound (II-A) were formed by irradiating the above hexane solution with ultraviolet rays having a wavelength of 350 to 400nm, and, among the resulted closed-ring forms, only the blue one was extracted by the column

chromatography. The extracted closed-ring form was dissolved into the hexane solution again, and then the closed-ring single crystal (II-B) was obtained from this solution by the solvent evaporation method.

[0024] The melting point of the open-ring form (II-A) was 139°C and that of the closed-ring form (II-B) was 193°C. The melting point of the closed-ring form (II-B) went down to 130°C when it was irradiated with visible light having a wavelength of 500nm or less. On the other hand, when the open-ring form (II-A) was irradiated with ultraviolet light having a wavelength of 350 to 400 nm, its melting point went up to 193°C. The behavior of the melting point to irradiation of light is illustrated in Fig. 1a. This behavior of the melting point was almost the same as that of the mixture of both crystals (II-A) and (II-B) as shown in Fig. 1b.

## Example 2

[0025] The closed-ring forms of the compound (III) were produced from a solution of compound (III) in hexane by irradiating the solution with ultraviolet rays having a wavelength of 313nm. Among the resulted closed-ring forms, only the red one (III-B) was extracted by the column chromatography. The extracted closed-ring form was dissolved in hexane again, and then the closed-ring single crystal (III-B) was obtained from this solution by a solvent evaporation method.

[0026] When the closed-ring form (III-B) was irradiated with visible light having a wavelength of 450nm or more at a room temperature for 30 minutes, its crystal melted. Furthermore, when the irradiation was continued on, the closed-ring form was recrystallized. It was thus apparent that the closed-ring form melted and recrystallized by irradiation of light.

[0027] It was apparent also from Figs. 1a and 1b that the melting point of the compound varies depending on the mixing ratio of the open-ring form and the closed-ring form. The physical properties of the compound, such as the refractive index and the like, vary in cases that the compound is completely in liquid phase, completely in solid phase, or in solid-liquid mixed phase, and it is possible to take advantages of this feature of the compound to compose optical memory devices or display devices. For example, when the compound (II) which is composed fully of the open-ring form is irradiated with ultraviolet rays, while being kept at 135°C, so as to transform 15% of its component to the closed-ring form, the composition (mixture) becomes liquefied and changes in physical property, such as the refractive index and the permeability, from the original state. It is possible to take advantages of such changes of the physical properties of the compound to compose optical memory devices and display devices.

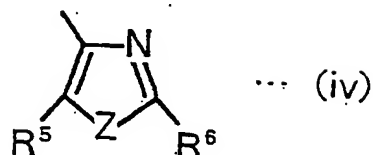
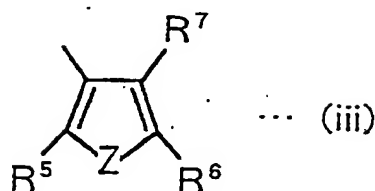
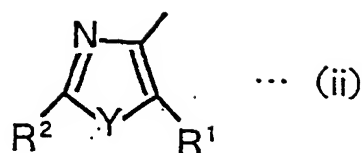
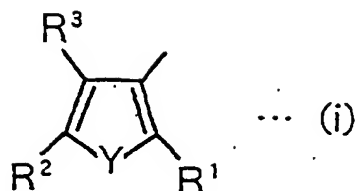
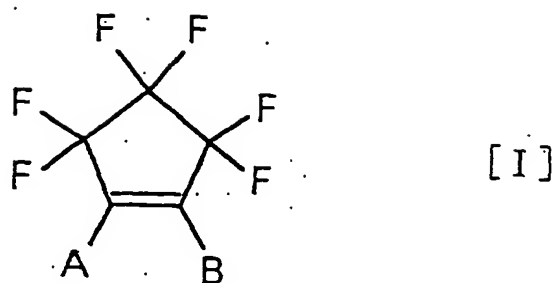
## Industrial Applicability

[0028] Since the diheteroarylethene-based compound of the present invention reversibly changes in color with light irradiation and also changes in phase from the open-ring form in the crystalline state to the closed-ring form in the crystalline state, or from the closed-ring form in the crystalline state to the open-ring form in the crystalline state via the liquid state, the compound can be applicable to optical recording media, display panels, sensors, optical switch devices and the like, by taking advantages of its variations in color and also its changes in physical property, such as the refractive index and the permeability, with its changes in phase.

[0029] When the compound in the liquid state or in the solid-liquid mixed state is to be used for such applications as above, it may be sealed in a glass cell which is divided in many rooms in a grid-like arrangement or in a stripe-like arrangement, or sealed in glass cells which are independent of each other.

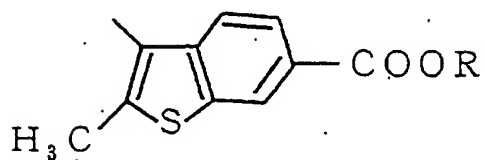
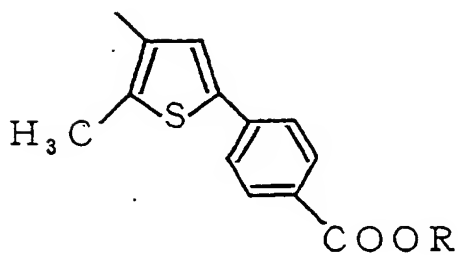
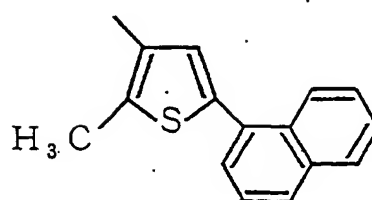
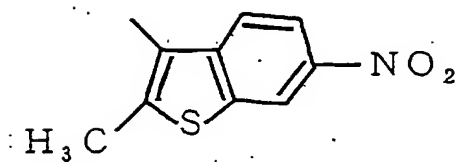
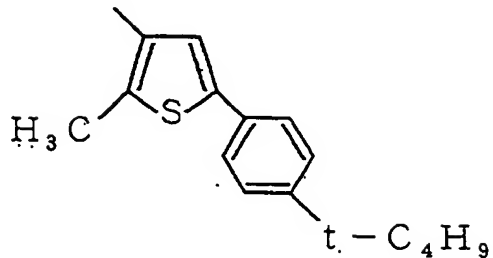
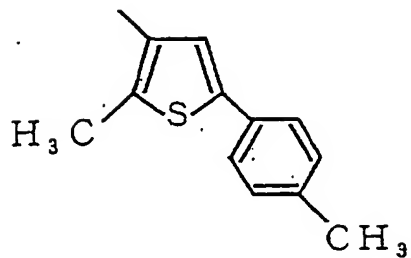
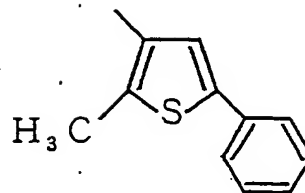
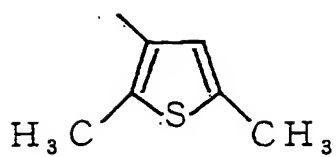
## Claims

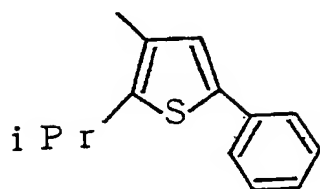
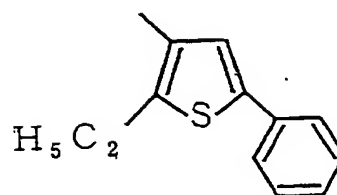
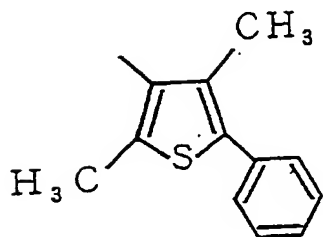
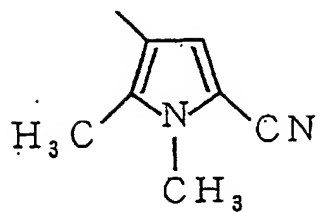
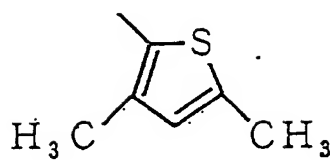
1. A photo-induced phase transition organic material composed of a diheteroarylethene-based compound within which the photochromic reaction occurs in the crystalline state.
2. A photo-induced phase transition organic material as claimed in claim 1, wherein said diheteroarylethene-based compound is the one expressed by the following general formula [I]:



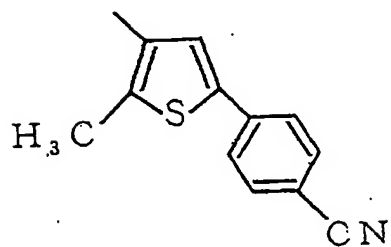
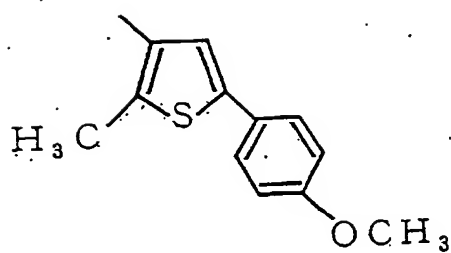
In the general formula [I], "A" expresses a substituent (i) or (ii). In the substituents (i) and (ii), "R<sup>1</sup>" expresses an alkyl group, an alkoxy group, a halogen atom, a trifluoromethyl group, a cyano group, or an aryl group which may have at least one substituent. "R<sup>2</sup>" and "R<sup>3</sup>" express a hydrogen atom, an alkyl group, an alkoxy group, a halogen atom, a trifluoromethyl group, a cyano group, or an aryl group which may have at least one substituent, respectively, wherein "R<sup>2</sup>" and "R<sup>3</sup>" are independent of each other. Alternatively, "R<sup>2</sup>" and "R<sup>3</sup>" are bonded to be a carbocyclic ring which may have at least one substituent, or a heterocyclic ring which may have at least one substituent. "Y" expresses —O—, —S—, or —NR<sup>4</sup>— in which "R<sup>4</sup>" expresses a hydrogen atom, an alkyl group which may have at least one substituent, an aryl group which may have at least one substituent, or a cycloalkyl group which may have at least one substituent. "B" expresses a substituent (iii) or (iv). In the substituents (iii) and (iv), "R<sup>5</sup>" expresses an alkyl group, an alkoxy group, a halogen atom, or a trifluoromethyl group. "R<sup>6</sup>" and "R<sup>7</sup>" express a hydrogen atom, an alkyl group, an alkoxy group, a halogen atom, a trifluoromethyl group, a cyano group, or an aryl group which may have at least one substituent, respectively, wherein "R<sup>6</sup>" and "R<sup>7</sup>" are independent of each other. Alternatively, "R<sup>6</sup>" and "R<sup>7</sup>" are bonded to be a carbocyclic ring which may have at least one substituent, or a heterocyclic ring which may have at least one substituent. "Z" expresses —O—, —S—, or —NR<sup>4</sup>— in which "R<sup>4</sup>" expresses a hydrogen atom, an alkyl group which may have at least one substituent, an aryl group which may have at least one substituent, or a cycloalkyl group which may have at least one substituent.

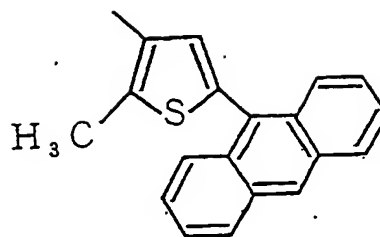
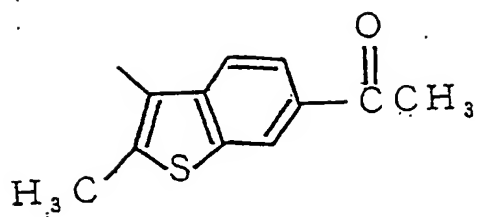
3. A photo-induced phase transition organic material as claimed in claim 2, wherein each of said substituents A and B is selected from the following substituents in which "R" expresses an alkyl group or a phenyl group:



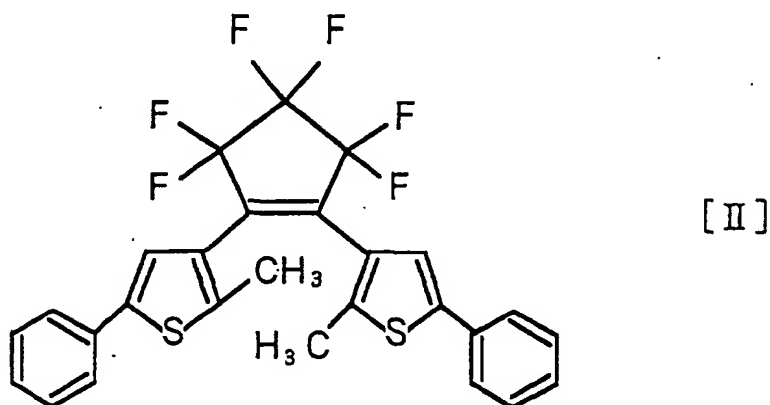


(iPr=isopropyl)

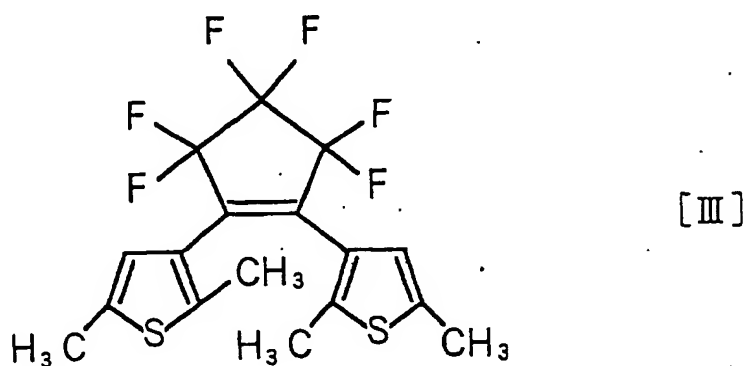




4. A photo-induced phase transition organic material as claimed in claim 3, wherein the diheteroarylethene-based compound is 1,2-bis(5-phenyl-2-methylthiophene-3-yl)perfluorocyclopentene as expressed by the following formula [II]:



5. A photo-induced phase transition organic material as claimed in claim 3, wherein the diheteroarylethene-based compound is 1,2-bis(2,5-dimethylthiophene-3-yl)perfluorocyclopentene as expressed by the following formula [III]:



6. A photo-induced phase transition organic material as claimed in any one of claims 1 through 5, wherein the diheteroarylethene-based compound is to be transferred in phase from the open-ring form to the closed-ring form with ultraviolet irradiation, and to be transferred in phase from the closed-ring form to the open-ring form with visible-light irradiation.



Fig. 1a

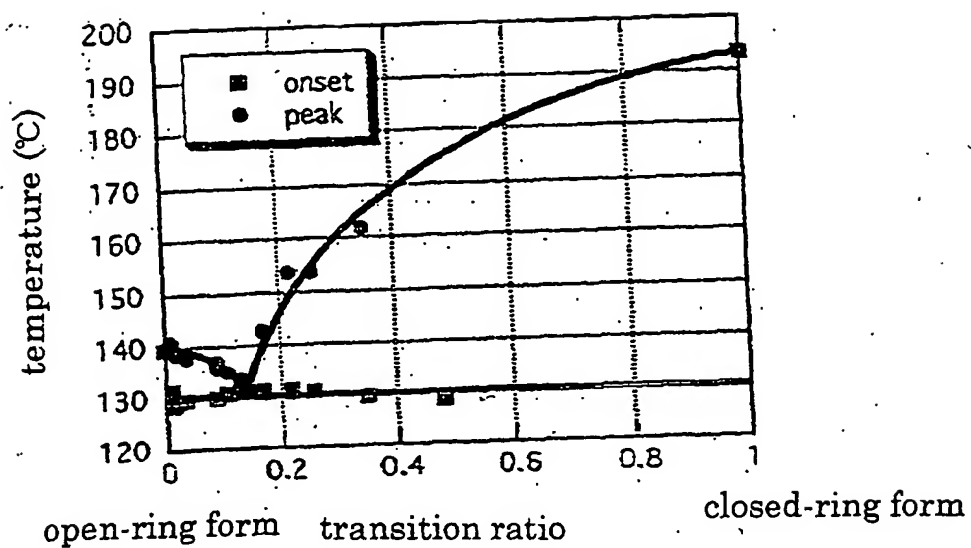
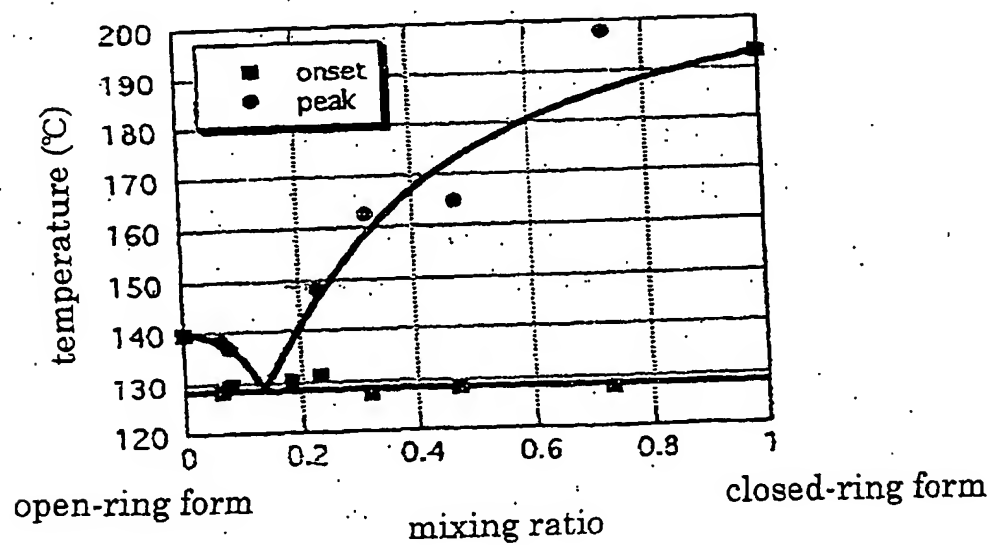


Fig. 1b



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/01330

## A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl.<sup>7</sup> C09K 9/02 // C07D 333/12, G02B 5/23, G02F 1/17

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl.<sup>7</sup> C09K 9/02, C07D 333/12, G02B 5/23, G02F 1/17

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
CA (STN), REGISTRY (STN)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	HIROSHI MIYASAKA et al., Picosecond laser photolysis studies on a photochromic dithenylethene in solution and in crystalline phases, Chemical Physics Letters, 1997, Vol.269, No.314, pages 281-285	1-6
X	JP, 10-251630, A (Masahiro IRIE), 22 September, 1998 (22.09.98), Claims; Par. No. [0007]; examples (Family: none)	1-6
X	JP, 9-241625, A (Masahiro IRIE), 16 September, 1997 (16.09.97), Claims; examples (Family: none)	1-4, 6
X	JP, 8-119963, A (Masahiro IRIE), 14 May, 1996 (14.05.96), Claims; examples (Family: none)	1-3, 6
P, X	JP, 11-255764, A (Japan Science and Technology Corp.), 21 September, 1999 (21.09.99), Claims; examples (Family: none)	1-6

☒ Further documents are listed in the continuation of Box C.☐ See patent family annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not  
considered to be of particular relevance"E" earlier document but published on or after the international filing  
date"L" document which may throw doubts on priority claim(s) or which is  
cited to establish the publication date of another citation or other  
special reason (as specified)"O" document referring to an oral disclosure, use, exhibition or other  
means"P" document published prior to the international filing date but later  
than the priority date claimed"T" later document published after the international filing date or  
priority date and not in conflict with the application but cited to  
understand the principle or theory underlying the invention"X" document of particular relevance; the claimed invention cannot be  
considered novel or cannot be considered to involve an inventive  
step when the document is taken alone"Y" document of particular relevance; the claimed invention cannot be  
considered to involve an inventive step when the document is  
combined with one or more other such documents, such  
combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search  
18 May, 2000 (18.05.00)Date of mailing of the international search report  
30.05.00Name and mailing address of the ISA/  
Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/01330

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	JP, 11-311813, A (Kyocera Corporation), 09 November, 1999 (09.11.99), Claims; examples (Family: none)	1-3, 5-6
P,X	JP, 2000-47270, A (Kyocera Corporation), 18 February, 2000 (18.02.00), Claims; examples (Family: none)	1-3, 5-6
E,X	JP, 2000-87024, A (Japan Science and Technology Corp.), 28 March, 2000 (28.03.00), Claims; examples (Family: none)	1-2, 6

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